

# Optimization of Synthesis and Characterization of Cassava Starch-graft-Poly(acrylonitrile) Using Response Surface Methodology

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**ABSTRACT:** Graft copolymerization of poly(acrylonitrile) onto cassava starch was carried out with potassium persulphate (PPS) as the free radical initiator using a response surface Box–Behnken design. Different levels of monomer concentration, initiator concentration, and temperature were used, and regression models were generated in terms of these factors, which can be used to predict the grafting level and efficiency at a given level of the factors. The grafted starches were characterized by FTIR, XRD, and SEM analyses and determination of %grafting (%G), N-content, thermal properties, water and saline solution retention, and rheological properties. Under the conditions used, %G was found to depend only on the temperature used for the reaction. The maximum %G of 120.1 was obtained for the sample synthesized under the following conditions: weight of AN = 0.753 mol/10 g starch, weight of PPS = 0.284 g and temperature = 55°C,

and the grafting efficiency was 30.03%. The absorption bands at 2243  $\text{cm}^{-1}$  for the nitrile group ( $-\text{CN}$ ) in the FTIR spectra of the products confirmed the grafting reaction. There was a decrease in crystallinity and disappearance of the granular structure after grafting of the starch. The melting temperatures of the graft copolymers determined by differential scanning calorimetry analysis were higher than that of the native starch. The grafted starches exhibited very high thermal stability as observed from the thermogravimetric analysis. The superabsorbent polymer prepared from the grafted starch by alkali saponification exhibited a maximum water absorbency of 636 g/g. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1546–1555, 2011

**Key words:** graft copolymerization; cassava starch; acrylonitrile; response surface design; thermal properties; glass transition temperature; superabsorbent polymer

## INTRODUCTION

There has been considerable interest in the recent years in the development of carbohydrate polymers with the capacity of creating effective functional groups for potential end use. Starch is a widely used natural biopolymer, which finds application in various industries such as textile, paper, adhesives, and food. Among the various modifications of starch, graft copolymerization with vinyl monomers appears to be a very fascinating field for research with unlimited possibilities for improving starch properties without sacrificing its biodegradable nature.<sup>1</sup> A number of graft copolymers have been prepared by grafting different monomers onto starch, which are gaining increasing importance in the manufacture of natural biodegradable polymer based

plastics, ion-exchange resins, and cosmetics.<sup>2–6</sup> Graft copolymerization imparts increased hydrophilicity, hydrophobicity, or polyelectrolyte nature to starch depending on the reagent and conditions used.

Graft copolymerization of acrylonitrile and methyl methacrylate onto native starch under the initiating of manganic ions was reported.<sup>7,8</sup> Patel et al.<sup>9</sup> reported the optimum conditions for the graft copolymerization of sodium salt of partially carboxymethylated amylose from potato starch with acrylonitrile. Effects of reaction medium on grafting of acrylonitrile onto sodium salt of partially carboxymethylated amylose were also studied.<sup>10</sup> Gao et al.<sup>11</sup> studied the initiating ability of potassium permanganate in the graft copolymerization of acrylonitrile onto corn starch. The results indicated that the grafting parameters, such as concentrations of potassium permanganate, acrylonitrile, starch, and catalyst acids, had significant effects on the graft copolymerization and the components of the graft copolymers. The most important application of starch-graft-poly(acrylonitrile) is in the development of superabsorbent polymers by alkali saponification.<sup>12</sup>

Cassava starch is one of the most important starches in industry with unique functional

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properties such as bland taste, high viscosity, good paste clarity, and low retrogradation. Because of the absence of any extraneous compounds in cassava tubers, the extraction of starch is comparatively easier, and the obtained product is very pure. However, in Indian markets, cassava starch has great competition from maize starch. Hence, the development of suitable modified starches from cassava can result in increased utilization of this starch. Systematic studies on the graft copolymerization of vinyl monomers onto cassava starch are scanty. In our previous works, we have reported the graft copolymerization of poly(acrylamide) onto cassava starch and the structural, thermal, and rheological properties of the grafted starches.<sup>13,14</sup> Literature on the modeling of grafting reactions of starch are also very few. The present study was an attempt to synthesize water-insoluble cassava starch-*graft*-poly(acrylonitrile) using potassium persulphate (PPS) initiator to optimize the reaction conditions for maximum grafting to develop prediction models in terms of the reaction conditions and also to characterize the graft copolymers by determining their structural and functional characteristics.

## MATERIALS AND METHODS

Cassava starch was extracted from freshly harvested tubers according to standard procedure.<sup>15</sup> Acrylonitrile, PPS, and potassium bromide were obtained from Sigma Aldrich Chemicals (St. Louis, USA).

### Synthesis of starch-g-copolymers

The graft copolymerization was carried out by the free radical initiated polymerization reaction of the pregelatinized cassava starch with acrylonitrile under different conditions of monomer concentration, initiator concentration, and temperature. PPS was used as the free radical initiator.<sup>16,17</sup> A response-surface Box-Behnken design for three variables was used for graft copolymerization, which involved 15 treatments with the central point replicating thrice. The variables and their levels used were as follows: weight of monomer ( $X_1 = 0.377, 0.565, \text{ and } 0.753 \text{ mol}/10 \text{ g}$  of starch in 200 mL water), weight of PPS ( $X_2 = 0.203, 0.284, \text{ and } 0.365 \text{ g}$ , i.e., 0.005, 0.007, and 0.009 mol/L), and temperature ( $X_3 = 35, 45, \text{ and } 55^\circ\text{C}$ ). Starch (10 g) was dispersed in 200 mL of distilled water with constant stirring and heated in a boiling water bath to gelatinize the starch. It was then cooled and placed in a constant temperature water bath maintained at the required temperature, and nitrogen gas is purged through the solution. PPS was then added and stirred, which was followed by the addition of required quantity of acrylonitrile. The reaction mix-

ture was stirred for 2 h under nitrogen atmosphere. The reaction was terminated by pouring the reaction mixture into methanol to precipitate the product. The crude polymer was then freed from the homopolymer by extraction with DMF for 48 h.<sup>18</sup> The residue was then dried and weighed.

### Percentage grafting and grafting efficiency

The percentage grafting and grafting efficiency were calculated as follows:<sup>16</sup>

$$\% \text{ Grafting} = [(W_1 - W_0)/W_0] \times 100$$

$$\% \text{ Efficiency} = [(W_1 - W_0)/W_2] \times 100$$

where  $W_0$ ,  $W_1$ , and  $W_2$  denote the weights of the original starch, grafted starch, and the monomer used, respectively.

### FTIR analysis

Infrared spectra of the native starch and grafted copolymers were recorded on a Perkin-Elmer FTIR instrument (Spectrum RX1) using a diffused reflectance accessory, which involves focusing a beam of infrared energy onto the powdered sample and then measuring the spectrum of the scattered radiation. The background spectrum was that of KBr.

### Scanning electron microscopy

The scanning electron micrographs of the native starch and the grafted copolymers were obtained after coating the specimens with gold films, using a JEOL/EO (Model JSM-6390) scanning electron microscope (JEOL, Tokyo, Japan) operating at 15 kV.

### X-ray diffraction analysis

The powder X-ray diffraction patterns of the native cassava starch and selected samples from the graft copolymers were obtained using a Bruker X-ray diffractometer (Model D8 Advance, Bruker AXS, Madison, WI) with Cu ( $K\alpha$  radiation  $\lambda = 1.5406 \text{ \AA}$ ) source.

### CHN analysis

The elemental analysis of the native starch and the graft copolymers was done using a Vario EL III CHNS elemental analyzer (Elementar Analysensysteme GmbH, Germany).

### Differential scanning calorimetry

The differential scanning calorimetry (DSC) was performed according to a reported procedure.<sup>1</sup> The

pure granular cassava starch and the graft copolymer (3–4 mg) were weighed out into aluminum pans and sealed hermetically. The samples were then tested in a Mettler Toledo DSC 822e instrument (Mettler-Toledo, Schcoerfenbach, Switzerland). An empty pan was used as reference, and the sample was heated from 40 to 275°C at a heating rate of 20°C/min under nitrogen atmosphere. Temperatures corresponding to the onset of transition, midpoint of the transition region, and enthalpy ( $\Delta H$ ) were recorded by means of the built-in software. To check the re-association of the molecules during cooling, heating–cooling–reheating cycle was performed as follows: heating from 30 to 250°C at 20°C/min, cooling back to 40°C, and reheating to 250°C at 20°C/min.

### Thermogravimetric analysis

Thermogravimetric analysis of the polymers was carried out on a Diamond TG/DTA analyzer (Perkin-Elmer, Shelton, CT). Heating was performed from 40 to 630°C at 10°C/min.

### Water and saline retention

Water and saline solution retention properties of the native starch and the graft copolymers were determined at ambient temperature according to the procedure of Kiatkamjornwong et al.<sup>19</sup> The samples (500 mg) were allowed to swell in distilled water (50 mL) for 24 h. The swollen copolymer gel was weighed. The water absorption capacity (WAC) was calculated as the weight of the water absorbed per gram of the materials. Saline solution retention capacity was determined by using 1% aqueous sodium chloride solution.

### Rheological properties

The dynamic rheological properties of the grafted starches were determined using a Physica VT2 Rheometer (Anton Paar Germany GmbH, Ostfildern, Germany) at 30°C, using a parallel plate system (PP20-SN5912, 1 mm diameter) at 1 mm gap. A weighed quantity of graft copolymer (2 g) was soaked in 20 g distilled water overnight to get a 10% gel. The mechanical spectra were obtained from frequency sweeps over the range of 0.10–10 Hz at a constant strain of 1%. The storage modulus ( $G'$ ), loss modulus ( $G''$ ), and phase angle ( $\delta$ ) were recorded, and the measurements were done in triplicate.

### Saponification of the grafted starch

Selected samples from the grafted starches with higher %G were saponified with 5% sodium hydroxide solution at 80–85°C for 90 min. The saponified

product was precipitated in methanol, and pH was adjusted to 6.5 using glacial acetic acid and dried. To determine the WAC, 100 mg of the sample was allowed to swell in 100 mL of distilled water at room temperature (30°C  $\pm$  2°C) for 1 h. The WAC was calculated from the weights of the dry sample and the swollen hydrogel.<sup>5</sup>

### Statistical analysis

All the determinations were performed in triplicate, and the data were analyzed using the package SAS 9.2 to perform ANOVA and to fit prediction models.<sup>20</sup> The treatments are considered significantly different at 5% level of significance ( $P \leq 0.05$ ). The response surface figures were generated using SAS. Simple correlation analysis was done to study the correlation between the percentage grafting and the observed properties of the grafted starches.

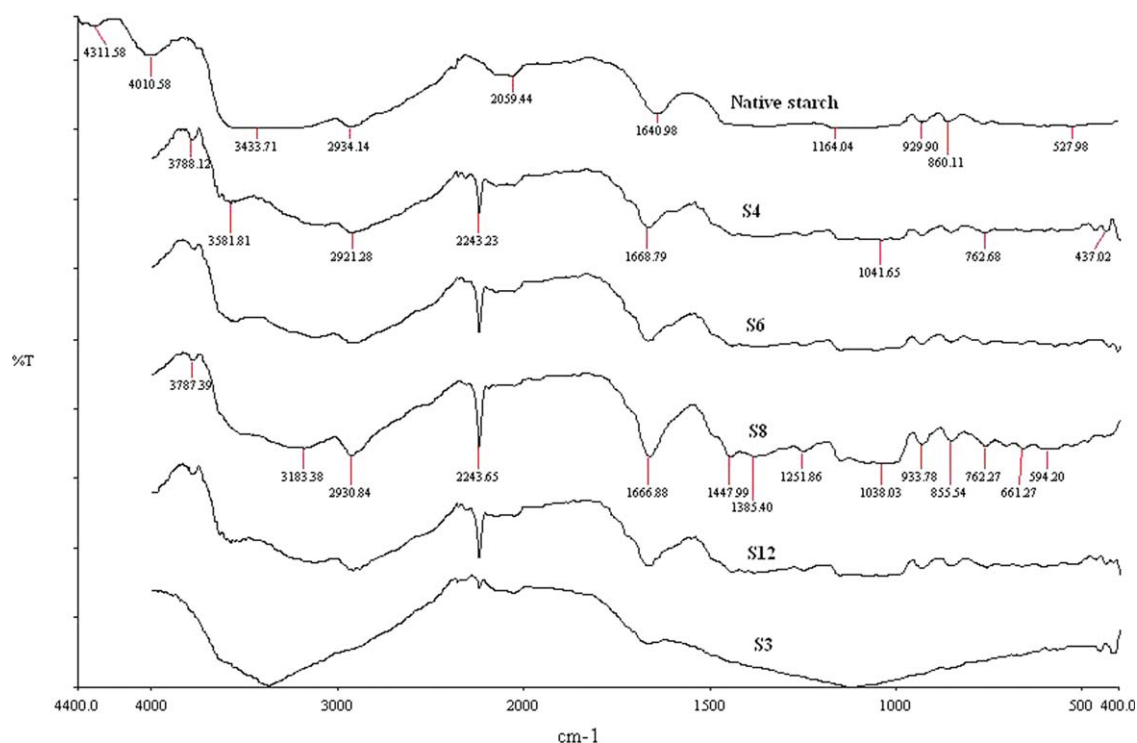
## RESULTS AND DISCUSSION

### FTIR analysis

Grafting onto cassava starch was confirmed by comparing the FTIR spectra of the native cassava starch with those of the grafted starches (Fig. 1). The IR spectrum of the native starch displayed the O–H stretching absorption in the region of 3390  $\text{cm}^{-1}$ , C–H stretching at 2932  $\text{cm}^{-1}$ , C=O stretching at 1647.7  $\text{cm}^{-1}$ , and the triplet band for the C–O–C stretching absorption at 1159, 1084, and 1013  $\text{cm}^{-1}$ . The spectra of the grafted copolymers also showed all the absorption bands, which are characteristic of the starch backbone. In addition, for the graft copolymers, the characteristic absorption bands at 2243  $\text{cm}^{-1}$  for the nitrile group ( $-\text{C}\equiv\text{N}$ ) was observed, furnishing thereby the evidence that grafting of acrylonitrile has occurred.

### Nitrogen content

Elemental analysis showed that N-content in the grafted starches ranged from 0.61  $\pm$  0.120 to 15.15  $\pm$  0.321% (Table I). Sample  $S_8$  with the highest % grafting had the highest N-content. Analysis of the data showed that among the different reaction parameters, initiator concentration and temperature had significant linear effects ( $P < 0.05$ ) on N-content in the grafted starches. The samples synthesized at higher levels of temperature showed higher N-content. Temperature and concentration of AN showed quadratic effects, which increased with the increase in these parameters, reached a maximum, and, with further increase in the variables, there was a decrease in %N. The quadratic regression equation for N-content in terms of significant effects is shown



**Figure 1** FTIR spectra of native cassava starch and starch-*graft*-poly(acrylonitrile). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in eq. (1), and it could explain about 94% of the total variations observed for %N.

$$\begin{aligned} \%N &= 39.98 + 20.97X_2 - 2.425X_3 + 8.10X_1^2 + 0.031X_3^2 \\ R^2 &= 0.94 \end{aligned} \quad (1)$$

A highly significant ( $P < 0.0001$ ) positive correlation was observed between %N and percentage

grafting as well as %N and grafting efficiency with correlation coefficients of 0.99 and 0.94, respectively.

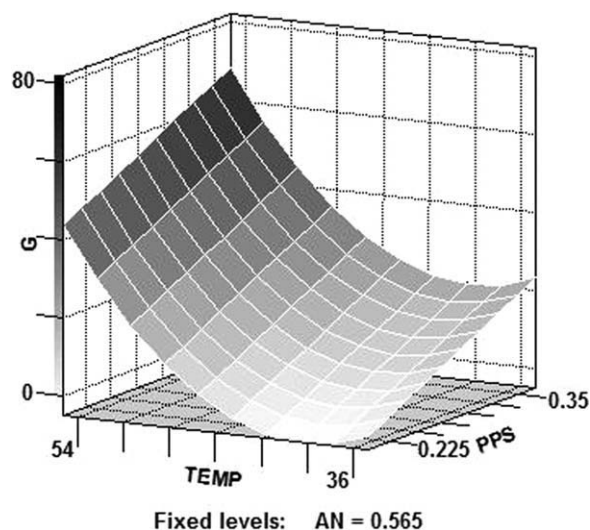
#### Effect of reaction variables on grafting

The %grafting and grafting efficiency of the copolymers synthesized under different reaction conditions are presented in Table I. The %G of the grafted starches ranged from 4.1 to 120.1% and grafting

**TABLE I**  
The Percentage Grafting, Grafting Efficiency, and Nitrogen Content of Cassava Starch-*g*-Poly(acrylonitrile) Under Different Reaction Conditions

Sample	Conc. of AN (mol) <sup>a</sup>	Weight of K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (g) <sup>a</sup>	Temp (°)	%G	%GE	%N	Water retention (g/g)	Saline retention (g/g)
S <sub>1</sub>	0.377	0.203	45	15.73	7.87	2.10 ± 0.101	9.7 ± 0.85	11.2 ± 0.44
S <sub>2</sub>	0.377	0.365	45	14.72	7.36	1.84 ± 0.083	11.9 ± 1.10	12.3 ± 0.34
S <sub>3</sub>	0.753	0.203	45	14.65	4.88	1.66 ± 0.111	12.9 ± 0.65	12.5 ± 0.62
S <sub>4</sub>	0.753	0.365	45	44.90	11.23	6.09 ± 0.213	4.3 ± 0.84	4.3 ± 0.56
S <sub>5</sub>	0.377	0.284	35	13.28	6.64	1.61 ± 0.204	17.2 ± 0.78	17.3 ± 0.54
S <sub>6</sub>	0.377	0.284	55	62.30	31.14	8.52 ± 0.071	3.9 ± 0.53	4.6 ± 0.36
S <sub>7</sub>	0.753	0.284	35	16.40	5.47	3.22 ± 0.620	8.9 ± 1.13	8.3 ± 0.34
S <sub>8</sub>	0.753	0.284	55	120.10	30.03	15.15 ± 0.321	2.1 ± 0.66	2.1 ± 0.74
S <sub>9</sub>	0.565	0.203	35	4.10	1.37	0.61 ± 0.120	17.8 ± 0.56	12.3 ± 0.69
S <sub>10</sub>	0.565	0.203	55	11.80	2.95	0.96 ± 0.053	19.8 ± 0.80	16.5 ± 0.27
S <sub>11</sub>	0.565	0.365	35	13.86	3.47	0.98 ± 0.102	21.0 ± 0.97	16.3 ± 0.39
S <sub>12</sub>	0.565	0.365	55	80.70	26.90	10.00 ± 0.110	2.5 ± 0.81	2.5 ± 0.50
S <sub>13</sub>	0.565	0.284	45	9.90	3.30	0.95 ± 0.030	14.9 ± 0.96	5.5 ± 0.65
S <sub>14</sub>	0.565	0.284	45	9.50	3.16	0.91 ± 0.024	18.2 ± 0.43	6.4 ± 0.38
S <sub>15</sub>	0.565	0.284	45	9.40	3.10	0.90 ± 0.061	15.9 ± 1.10	6.1 ± 0.23

<sup>a</sup> The quantities of acrylonitrile and potassium persulphate were for 10g starch in 200ml water.



**Figure 2** Response surface plots showing the effect of variables on %G of cassava starch-g-poly(acrylonitrile).

efficiency from 1.37 to 31.14%. The percentage grafting was also calculated from the results of elemental analysis (data not shown). It was observed that, for some of the samples, the two values were in good agreement, whereas some of the sample showed comparatively lower values than those calculated from weight. The highest %G was obtained for sample  $S_8$ , which was synthesized under the following conditions: weight of AN = 0.753 mol/10 g starch, weight of PPS = 0.284 g, and temperature = 55°C.

#### %Grafting

Response surface methodology applied for the variables indicated that among the different factors used, %G was significantly affected by the concentration of the initiator and temperature. Temperature had significant linear and quadratic effects on %G ( $P < 0.05$ ). Therefore, %G was higher for the samples synthesized at higher temperatures (Table I). The linear effect of concentration of PPS also was significant resulting in higher %G at higher levels of the initiator. A quadratic model was fitted for %G as shown in eq. (2). Only significant effects were retained in the fitted model. The value of the coefficient of determination ( $R^2$ ) was calculated as 0.92 for percentage grafting. The equation explains 92% of the total variations for %G, which shows the high prediction performance of the proposed model.

$$\%G = 314.45 + 166.51X_2 - 18.16X_3 + 0.23X_3^2 \quad (2)$$

#### Grafting efficiency

The grafting efficiency was also higher at higher temperatures. The quadratic terms of concentration

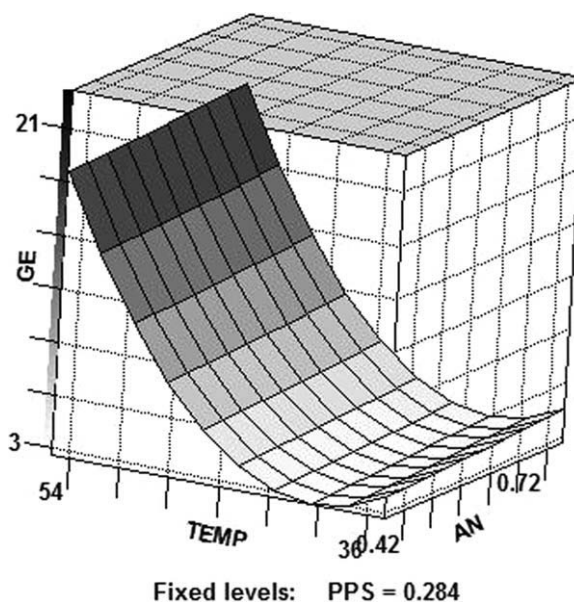
of acrylonitrile and temperature significantly ( $P < 0.05$ ) affected the grafting efficiency, which illustrates the presence of an optimum level of these two factors for getting maximum efficiency. The  $R^2$  was 0.92 for grafting efficiency, showing high prediction performance of the model. The quadratic regression model illustrates the behavior of GE as a function of significant factors as represented by eq. (3).

$$\%GE = 118.62 - 5.97X_3 + 1.8X_1^2 + 0.08X_3^2 \quad (3)$$

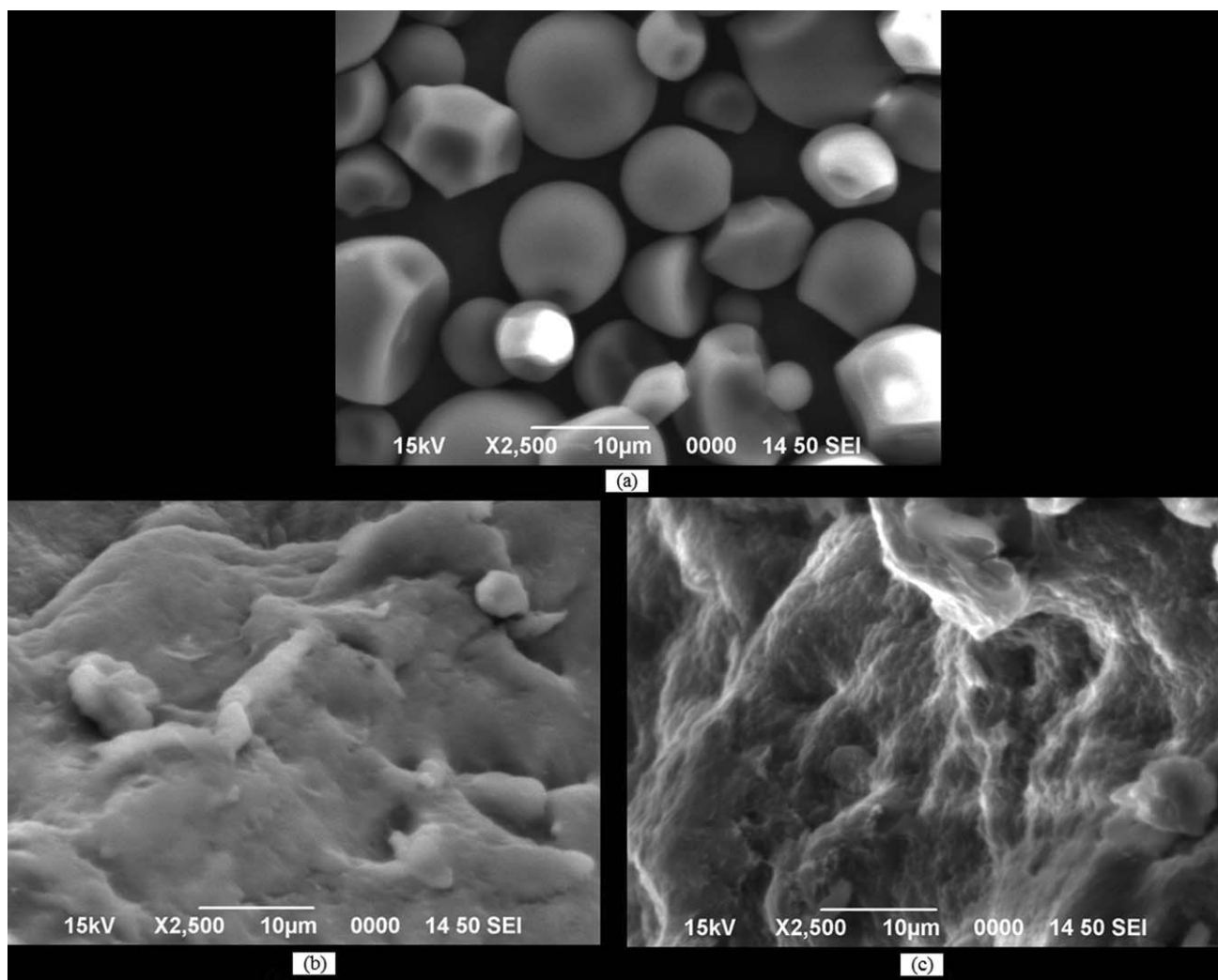
Using these regression equations, it is possible to predict the %G and GE values at a given level of the variables. The three-dimensional response surface plots for %G and %GE showing the relative effects of factors have been depicted in Figures 2 and 3, respectively.

#### Scanning electron microscopy

Scanning electron micrographs (SEM) of the granular native cassava starch and that of the graft copolymers  $S_4$  and  $S_8$  with different levels of %grafting are shown in Figure 4(a–c). The native cassava starch granules were mostly spherical in shape with a flat surface on one side containing a pit [Fig. 4(a)]. The micrographs showed that the granular structure has been completely disappeared in the grafted starches [Fig. 4(b,c)]. The surface appeared nonuniform and nonplanar in both the samples. SEM micrographs thus provided substantial morphological evidences in favor of grafting of acrylonitrile onto starch. Almost similar observation of decrease in uniformity and planarity



**Figure 3** Response surface plots showing the effect of variables on %GE of cassava starch-g-poly(acrylonitrile).



**Figure 4** Scanning electron micrographs of the native and grafted starches at different magnifications. (a) Native cassava starch and (b) and (c) grafted starches.

was reported for cassava and potato starches grafted with acrylamide and polyethylene.<sup>11,21,22</sup>

#### X-ray diffraction analysis

The XRD patterns of the native cassava starch and starch-*g*-poly(acrylonitrile) samples viz.,  $S_4$  (%G = 44.9),  $S_8$  (169.05), and  $S_{12}$  (80.7) are shown in Figure 5. The native starch showed  $C_A$ -type X-ray diffraction pattern with major peaks at diffraction angles,  $2\theta = 14.932^\circ$  ( $d = 5.928 \text{ \AA}$ ),  $17.141^\circ$  ( $d = 5.169$ ),  $18.058^\circ$  ( $d = 4.908$ ),  $22.989^\circ$  ( $d = 3.866$ ), and  $23.408^\circ$  ( $d = 3.797 \text{ \AA}$ ). Grafted starches displayed crystalline structures which differed from that of native starch. The XRD patterns of the graft copolymers showed B-type structure, with a characteristic peak at  $16.9^\circ$  ( $2\theta$ ). For the sample  $S_4$ , the intensity of this peak was comparatively lower. However, for  $S_8$  and  $S_{12}$ , the grafted starches with higher %grafting, and more intense peaks were observed. Similar types of

XRD patterns were reported for aged thermoplastic maize starch–zein blends, and they explained that this structure was preferentially formed by crystallization of the short outer chains of amylopectin.<sup>23</sup>

#### Differential scanning calorimetry

The melting temperatures of the grafted starches were determined by differential scanning calorimetry (DSC) studies (Table II). The midpoint in the DSC curve was taken as  $T_m$ , as it gives the average temperature at which most of macromolecules undergo the melting. In the DSC curves of the native starch as well as that of the graft copolymers, only one endotherm was observed in the temperature range used for the study (Fig. 6). The  $T_m$  of native cassava starch having about 8–10% moisture was  $162.5^\circ\text{C} \pm 1.65^\circ\text{C}$ . Most of the graft copolymers exhibited higher  $T_m$  than that of the native starch. The  $T_m$  values of the copolymers were in the range

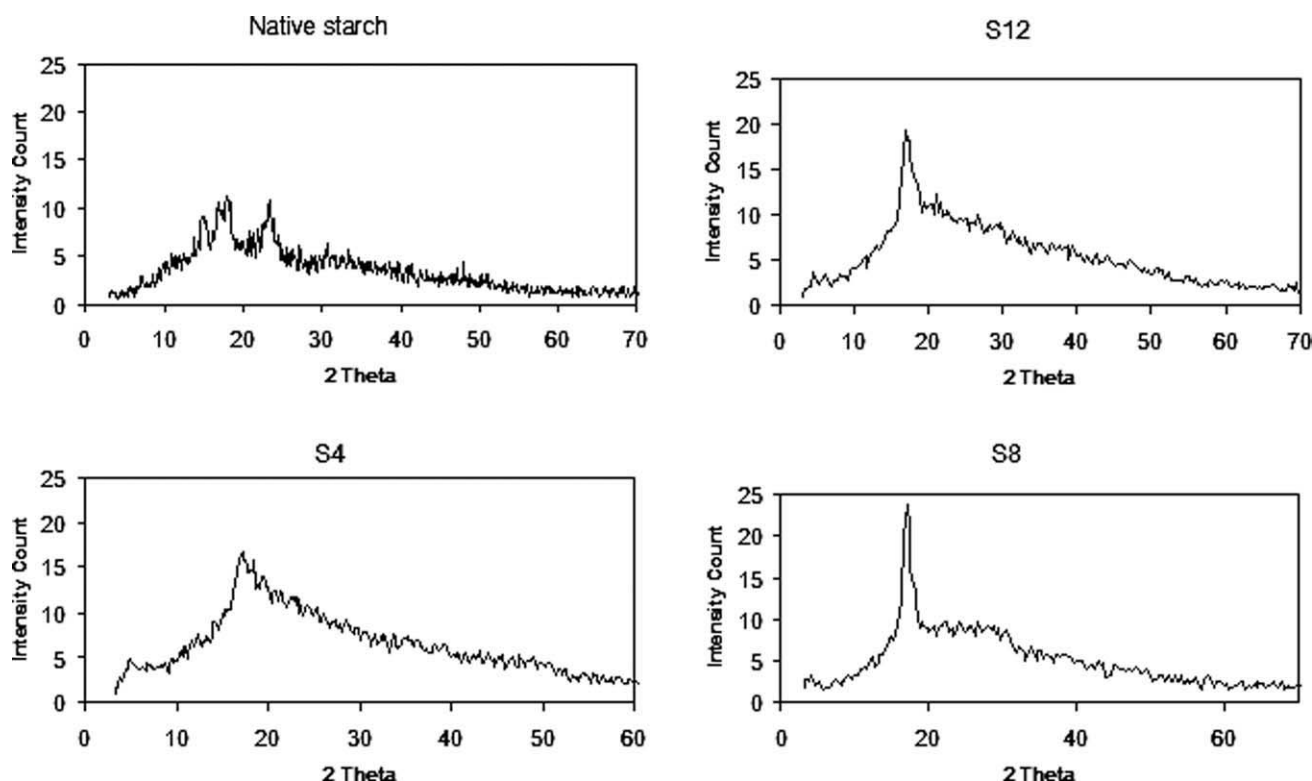


Figure 5 XRD patterns of the native and grafted starches.

$153.2^{\circ}\text{C} \pm 2.36^{\circ}\text{C}$  to  $181.8^{\circ}\text{C} \pm 2.13^{\circ}\text{C}$  (Table II). The rather large range in  $T_m$  could be the effect of varying levels of bound moisture in the grafted samples.

For the graft copolymers of starch with acrylamide, a decrease in glass transition ( $T_g$ ) was reported in comparison to the native cassava starch, and this was attributed to the internal plasticization effect of the monomers when grafted on to the starch.<sup>1,14</sup> In the present study, an increase in melting tempera-

ture was observed after grafting with poly(acrylonitrile). The higher temperature for these polymers shows more difficult molecular changes in comparison with graft copolymers with acrylamide.

For the acrylamide graft copolymers of cassava and maize starches, a second endothermic transition was observed in the DSC patterns, and this was attributed to the fusion of the crystallites.<sup>1,14</sup> However, for most of the AN-grafted starches, a second transition was absent in the temperature range used for the study.

The enthalpy of melting was  $138.6 \pm 3.01$  J/g for the native cassava starch. The graft copolymers

TABLE II  
DSC Parameters for Native Cassava Starch and Starch-g-poly (AN)

Sample	Onset of melting ( $^{\circ}\text{C}$ )	Midpoint ( $T_m$ ) ( $^{\circ}\text{C}$ )	$\Delta H$ (J/g)
Native starch	$160.3 \pm 1.25$	$162.5 \pm 1.65$	$138.6 \pm 3.01$
S <sub>1</sub>	$158.2 \pm 1.30$	$160.5 \pm 1.83$	$26.0 \pm 8.12$
S <sub>2</sub>	$173.4 \pm 2.21$	$176.7 \pm 1.77$	$33.6 \pm 6.17$
S <sub>3</sub>	$178.0 \pm 1.87$	$181.8 \pm 2.13$	$27.5 \pm 3.88$
S <sub>4</sub>	$146.2 \pm 3.19$	$153.2 \pm 2.36$	$21.1 \pm 1.32$
S <sub>5</sub>	$175.8 \pm 2.31$	$177.9 \pm 1.89$	$38.0 \pm 2.87$
S <sub>6</sub>	$164.1 \pm 3.15$	$167.6 \pm 2.55$	$54.2 \pm 4.12$
S <sub>7</sub>	$177.3 \pm 2.05$	$180.8 \pm 2.14$	$26.4 \pm 5.65$
S <sub>8</sub>	$173.1 \pm 2.10$	$176.5 \pm 2.54$	$26.7 \pm 2.10$
S <sub>9</sub>	$162.7 \pm 2.11$	$166.8 \pm 1.87$	$38.6 \pm 2.13$
S <sub>10</sub>	$166.4 \pm 1.76$	$171.1 \pm 1.95$	$17.4 \pm 3.12$
S <sub>11</sub>	$168.3 \pm 1.35$	$170.4 \pm 2.01$	$44.7 \pm 1.87$
S <sub>12</sub>	$176.9 \pm 2.55$	$181.5 \pm 2.36$	$18.1 \pm 2.08$
S <sub>13</sub>	$166.5 \pm 3.10$	$170.4 \pm 3.04$	$56.5 \pm 3.54$
S <sub>14</sub>	$161.8 \pm 2.97$	$165.3 \pm 2.40$	$60.2 \pm 5.02$
S <sub>15</sub>	$162.7 \pm 3.10$	$165.6 \pm 2.41$	$61.2 \pm 1.98$

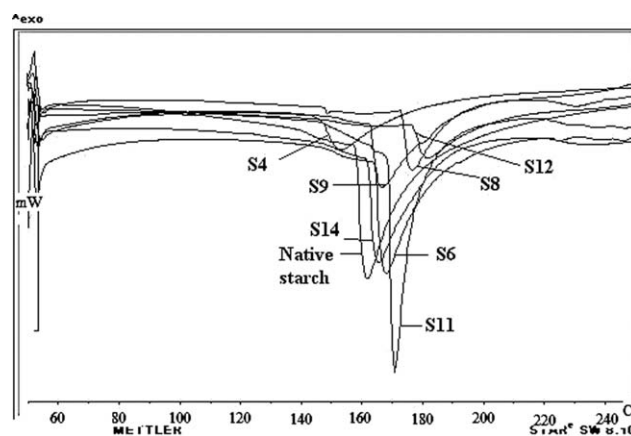
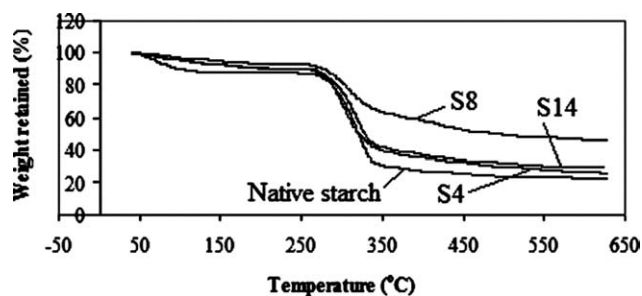


Figure 6 DSC curves for the native cassava starch and starch-graft-poly(acrylonitrile).



**Figure 7** Thermograms for native cassava starch and starch-graft-poly(acrylonitrile).

showed significantly lower values. A wide variation was noticed in the enthalpy of the grafted samples, which ranged from  $17.4 \pm 3.12$  to  $61.2 \pm 1.98$  J/g. The lowering in enthalpy for melting could be attributed to the change in crystallinity of starch on grafting of the monomers. Simple correlation analysis showed that none of the DSC parameters showed significant correlation to %G or other properties.

When the graft copolymers were subjected to heating-cooling-reheating cycle, no peaks were observed in the reheating phase indicating that the graft melting was not reversible.

### Thermogravimetric analysis

Thermogravimetric analysis was done for the native starch, and the grafted starch samples  $S_2$ ,  $S_4$ ,  $S_8$ ,  $S_9$ , and  $S_{14}$ . The unmodified cassava starch showed a three-step thermogram and the major weight loss of about 70% occurred at 275°C in the second step (Fig. 7). The weight retained at 622°C was 22%. In the case of grafted starches, the weight loss was gradual, and higher thermal stability than native starch was noticed (Fig. 7). The graft copolymers retained about 25–45% of the initial weight at 630°C. The sample  $S_8$  retained 45% of the initial weight at the end of the analysis showing very high thermal stability. According to earlier reports, the weight loss of PAN films and fibers were  $\sim 38.55$  and  $39.58\%$ , respectively, at 250°C, and the weight retention was about 50% at 600°C.<sup>24</sup> Therefore, the present study showed that incorporation of starch could retain the thermal stability of poly(acrylonitrile) polymer, and the weight retention of some of the starch-g-poly(acrylonitrile) samples at 630°C was almost similar to that of PAN.

The thermal behavior of graft copolymers of starch with poly(acrylamide) and poly(acrylonitrile) has been earlier studied by different researchers.<sup>14,25,26</sup> They have observed that copolymerization enhances the thermal stability of starch. Jyothi et al.<sup>14</sup> reported increased thermal stability for cassava starch, graft copolymerized with poly(acrylamide). The present

study showed that the thermal stability was more in the case of cassava starch-g-poly(acrylonitrile).

### Water and saline solution retention

The copolymers of starch with hydrophobic grafts such as starch-g-poly(acrylonitrile) are usually not dispersible in water. In this study too, it was observed that graft copolymers with higher grafting level did not undergo swelling in water, whereas those with very low levels of grafting underwent some extent of swelling when suspended in water for overnight. The water-absorption capacities of the starch-g-poly(acrylonitrile) samples were in the range of  $2.1 \pm 0.66$  –  $21.0 \pm 0.97$  g/g (Table I). The sample  $S_8$ , which exhibited highest %G, showed the lowest water retention capacity, whereas the highest value was shown by the sample  $S_{11}$  with a %G of 14.7. There was a significant positive correlation between %G and WAC. The water-retention capacity of the copolymers with lower levels of %G was found to be comparatively higher than that of the samples with higher %G. This is because the presence of more hydrophobic grafts results in lower water absorption. Analysis of the data showed that all the reaction conditions significantly affected the WRC of the grafted starches. Generally, WRC decreased with the increase in concentration of AN, PPS, and temperature, and it was lower for the grafted starches synthesized at higher levels of monomer concentration, initiator concentration, and temperature.

The saline retention ranged from  $2.1 \pm 0.74$  to  $17.3 \pm 0.54$  g/g. In this case also, the lowest value was shown by the sample  $S_8$ . The SRC also showed negative correlation to %G ( $r = 0.65$ ,  $P = 0.008$ ), and therefore, at higher levels of %grafting, the saline retention capacity was lower.

Similar results were reported earlier, and, on grafting poly(acrylonitrile), viscosity and shear stability of potato starch solutions increased while water and saline retaining ability decreased.<sup>27</sup>

Generally, copolymers of starch with hydrophobic grafts such as starch-g-poly(acrylonitrile) cannot be dispersed in water, but remains as grainy solids, even after prolonged heating. In our study too, we could not observe gelatinization of the grafted starches even after heating in water at 95°C.

### Rheological properties

The storage modulus of all the samples showed a slight increase with increase in frequency. However, the frequency dependence of  $G'$  was very small as seen from the lower positive slopes. The  $G'$  values ranged from 600 to 2510 Pa for the gels of the grafted starches except for  $S_4$ ,  $S_6$ ,  $S_8$ , and  $S_{12}$  at a



**TABLE III**  
**Mechanical Spectra and Exponents in Power Equation for the Dynamic Moduli of the Gels/Suspensions of Grafted Starches**

Sample	Storage modulus (at 10 Hz)	Loss modulus (Pa)	Phase angle (°)	Exponents in power equation <sup>a</sup>	
				$n'$	$n''$
S1	1890 ± 25.0	1240 ± 16.8	33.3 ± 1.10	0.124	0.103
S2	1191.5 ± 13.5	1105 ± 20.3	43.5 ± 2.32	0.266	0.173
S3	1470 ± 17.3	1050 ± 16.5	35.6 ± 2.51	0.334	0.166
S4	46,900 ± 82.0	7240 ± 12.6	8.77 ± 1.03	0.002	0.055
S5	1170 ± 16.8	1090 ± 21.4	43 ± 0.91	0.328	0.187
S6	52,200 ± 65.0	6880 ± 13.0	7.5 ± 2.20	0.021	0.063
S7	2510 ± 22.0	1200 ± 18.0	25.5 ± 1.62	0.164	0.017
S8	2350,000 ± 182.1	247,000 ± 210.0	6.0 ± 0.71	0.033	0.015
S9	55,300 ± 52.4	9560 ± 33.0	9.8 ± 1.01	0.139	0.019
S10	1500 ± 11.8	967 ± 15.3	32.8 ± 1.33	0.320	0.158
S11	753 ± 36.0	1040 ± 12.8	54.2 ± 1.40	0.359	0.207
S12	196,200 ± 121.5	28,800 ± 46.2	7.91 ± 0.81	0.124	0.057
S13	1090 ± 35.7	1080 ± 36.1	44.8 ± 3.82	0.342	0.196
S14	1270 ± 14.7	1290 ± 21.4	45.4 ± 2.91	0.363	0.198
S15	592 ± 42.0	1060 ± 23.1	44.9 ± 2.20	0.358	0.201

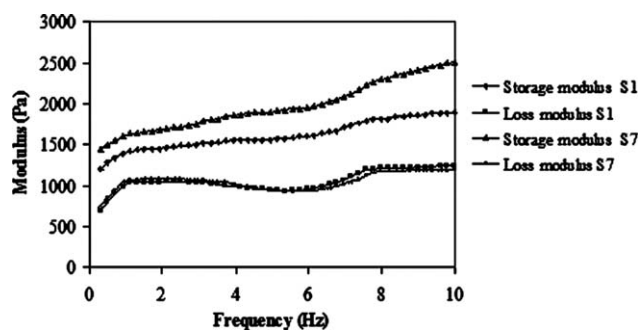
<sup>a</sup>  $r^2$  ranged from 0.703 to 0.985 for  $n'$  and 0.28 to 0.952 for  $n''$ .

frequency of 10 Hz. For the samples S<sub>4</sub>, S<sub>6</sub>, S<sub>8</sub>, and S<sub>12</sub>, it ranged from 46,900 to 2350,000 Pa (Table III). As mentioned earlier, among the grafted starches, samples S<sub>4</sub>, S<sub>6</sub>, S<sub>8</sub>, and S<sub>12</sub>, which had comparatively higher %grafting did not undergo swelling after soaking in water for overnight, possibly due to the higher level of hydrophobic grafts. Therefore, suspensions of these samples showed extremely different behavior for rheological properties in comparison with the rest of the samples, which underwent swelling to some extent due to lower levels of grafting. Generally, the less dependency of storage modulus on frequency explains the true gel characteristics of the samples, and the very high values of the same usually represent the more solid nature of the gels. However, in the present case, due to the hydrophobic nature of the grafts in the case of copolymers with high %G (S<sub>4</sub>, S<sub>6</sub>, S<sub>8</sub>, and S<sub>12</sub>), no swelling was actually taking place, and the polymer may be in a moistened state exhibiting no/very less viscoelastic properties.

Loss modulus was significantly lower than storage modulus for all the grafted starches throughout the frequency range. For all the samples, loss modulus showed a typical pattern of increase with increase in frequency at the initial levels (up to a frequency of about 1 Hz), then remained constant up to 2.5 Hz, which then decreased up to 5 Hz followed by a steady increase and finally attaining almost constant values (Fig. 8). This abnormal trend of  $G''$  with frequency also proved the moistened state of the grafted polymers without any gelling.

Because of the unusual behavior observed for these samples, power law equation was applied to

the data of dynamic moduli, using which the solid-to-liquid transition of a system can be ascertained. The frequency dependence of  $G'$  and  $G''$  ( $n'$  and  $n''$ , respectively) was determined from the power law relationship in the frequency sweep,  $G' = G'_o \omega^{n'}$  and  $G'' = G''_o \omega^{n''}$ , where  $G'_o$  and  $G''_o$  are the intercepts and  $\omega = 2\pi f$  is the frequency in rad s<sup>-1</sup>.<sup>28</sup> For  $n'$ , values close to 2 or 0, and for  $n''$ , values close to 1 or 0 represent liquid or solid behaviors, respectively. Table III shows the  $n'$  and  $n''$  for the dynamic moduli of the grafted starches. In the present case, the values of  $n'$  ranged from 0.002 to 0.363 and those of  $n''$  from 0.015 to 0.217. Because the values of  $n'$  and  $n''$  are close to 0, the samples exhibited a true solid nature. This also implies that the grafted polymers after water soaking did not show any viscoelastic properties.



**Figure 8** Plots showing the frequency dependence of dynamic moduli of representative samples of starch-g-poly(acrylonitrile).

Analysis of the data showed that none of the reaction factors have significant effect on storage modulus as well as loss modulus, whereas phase angle was significantly affected by the interaction effect of concentration of AN and temperature. The dynamic moduli were higher for the copolymers with higher levels of percentage grafting.

The dynamic-mechanical properties of the gels of cassava starch-*g*-poly(acrylamide) was earlier reported, and, unlike in the present case, they observed more liquidlike nature for the gels of those polymers, which contained water-soluble grafts.<sup>14</sup>

### Saponification of grafted starch

The grafted starches AP<sub>4</sub> (%G = 44.9), AP<sub>8</sub> (120.1), and AP<sub>12</sub> (80.7), which showed higher %G values, were subjected to saponification with sodium hydroxide to obtain highly water-absorbing polymers. The superabsorbent polymer developed from the grafted starch AP<sub>8</sub> exhibited a maximum WAC of 636 g/g after swelling for 1 h and that from AP<sub>4</sub> and AP<sub>12</sub> showed values of 492 and 525.5 g/g, respectively. It was observed that the water absorbency of the SAP was higher when %G of the corresponding grafted starch was higher. The deswelling pattern of the swollen polymer when kept open at ambient temperature was observed, and it was found that it released the bound water very slowly to the surroundings and became dry in about 10 days. Hence these polymers can be exploited in soil-conditioning applications and in agriculture mulches to preserve the soil moisture.

### CONCLUSIONS

Graft copolymers of cassava starch with acrylonitrile were synthesized by using PPS as free radical initiator. The reaction conditions were optimized, and the effects of factors on various properties of the copolymers were studied by a response surface methodology. Using the response surface models and regression equations generated using the experimental values, it is possible to predict the characteristics of the graft copolymers under a given set of variables. The copolymers exhibited very high thermal stability and did not gelatinize in water even at 95°C. These polymers can find application in fields, which require high thermal stability and hydrophobic characteristics. The superabsorbent polymers prepared from the grafted starches can be exploited in agriculture for soil moisture retention and in the develop-

ment of personal care products such as disposable diapers.

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